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Glyphosate Residues in Surface Water Following Initial Manfor Ltd. Field Trials, 1985

By A.E. Beck

Manitoba
Environment and
Workplace Safety
and Health

ERRATUM

Page 5, paragraph 2, sentence 4 should read:

"Unlike the Long Lake cutover, the Atik site had been planted with black spruce container stock in 1982."

GLYPHOSATE RESIDUES IN SURFACE WATER

FOLLOWING 1985 MANFOR LTD

FIELD TRIALS

A. E. Beck
Water Standards and Studies Section
Environmental Management Services Branch
Environmental Management Division

Water Standards and Studies Report #87-4
Manitoba Environment and Workplace Safety and Health

SUMMARY

Forestry management personnel of Manfor Ltd. conducted experimental field trials of the herbicide Roundup(R) during 1985. The trials, conducted at three sites near The Pas, were carried out to assess the efficacy of Roundup(R) for control of weed tree and shrub species on forestry plantations. Rates of aerial application were 1.08, 1.44 and 1.80 kg of active ingredient per hectare. Glyphosate is the active ingredient in Roundup(R).

A meager literature pertaining to the activity of glyphosate in aquatic systems, the absence of locally generated data and strong concerns among area residents, prompted Manfor Ltd. to enlist the aid of Manitoba Environmental Management Division for monitoring environmental impacts. The objective of the present study was to examine glyphosate residues in surface waters following application to experimental spray blocks. Issues examined included quantitation of residues, persistence and transport of residues from the target area. Utilization of external analytical facilities also required assessment of analytical capabilities.

Residues of glyphosate and AMPA, the major metabolite of glyphosate, were analyzed. The analytical detection limits, calculated from a series of blanks, were 2.2 µg/L for glyphosate and 9.05 µg/L for AMPA. Mean recovery rates for spiked samples was 115% for glyphosate residues. Recovery rates for AMPA residues could not be independently assessed because of a lack of stock chemical. These analytical capabilities were considered adequate for the purposes of the present study.

Quantitation of residues and assessment of persistence were hampered by limited ponded water located within the confines of the experimental spray blocks. However, maximum glyphosate residues of 1088 µg/L were detected within one pond less than 1-1/2 hours after spray. This value corresponded reasonably well to the 1.08 Kg/ha rate of application for the site. Maximum AMPA residues of 10.9 µg/L were detected at the same site 5 days after spray. Neither glyphosate nor AMPA residues were detected 30 days after spray.

Glyphosate residues were observed to dissipate much more rapidly than had been indicated by most literature references. A half-life of less then 24 hours was indicated for glyphosate applied aerially under local conditions. Minimal and infrequent detections of AMPA precluded definition of dissipation rates for this metabolite.

Transport of glyphosate and AMPA residues to aquatic systems outside of the target area was limited to drift during and immediately following aerial application. Evidence of other transport mechanisms was not encountered at any of the 19 peripheral sampling sites.

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1.0 INTRODUCTION

Glyphosate or Roundup(R)* (N-(phosphonomethyl)glycine) was first described as a herbicide in 1971 (Baird et al, 1971). It has a high level of broad-spectrum, non-selective, post-emergence activity (Franz, 1971). This means that when applied to foliage, it is toxic to essentially all annual and perennial plants. Because glyphosate is tightly bound to soil particles and is rapidly metabolized by soil microflora, it has little residual soil activity (Sprankle et al, 1975; Sacher, 1978). Thus it is particularly suitable for a variety of agricultural applications and is widely used in the industry.

A few plants, such as dormant conifers, show exceptional resistance to foliage treatment due to a low degree of uptake and transport (Franz, 1971). This resistance indicated potential for forestry use of glyphosate as a selective herbicide for the removal of unwanted vegetation. Accordingly, glyphosate has been used with increasing frequency in the Pacific northwest and to a more limited degree in the east (Ghassemi et al, 1982). Favourable toxicological studies (Folmar et al, 1979; Sullivan and Sullivan, 1979; Hildebrand et al, 1980; 1982; Sullivan et al, 1981) and successful forestry applications elsewhere induced forestry management personnel of Manfor Ltd. to propose experimental field trials during the 1984 season. The trials were proposed for plantations located near The Pas (53° 50", 101° 15') in order to assess the efficacy of glyphosate under local conditions.

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* Roundup(R) is a registered trademark of Monsanto Co., St. Louis, Mo, USA.

The proposed experimental field trials aroused a concern among local residents in the Summer of 1984. The imminence of the proposed application date and the relatively short term period during which glyphosate may successfully be applied, precluded organization of adequate environmental monitoring and information dissemination programs. Hence, the proposed 1984 field trials were cancelled and alternate plans were formulated for the 1985 season.

The purpose of the present study was to examine glyphosate residues in surface waters following the 1985 field trials. The dearth of references pertaining to the activity of glyphosate in aquatic systems and the absence of local data, necessitated a general approach to monitoring. Broad issues examined included order of magnitude quantitation of residues, general persistence and indications of export from the target area. All objectives were restricted to the aquatic system.

2.0 DESCRIPTION OF THE STUDY AREA

The area lies within the paleozoic geological subdivision (Weir, 1983). Soils are of the eutric brunisol and organic groups (Ibid). Northern coniferous forest constitutes the natural vegetation of the area. The topography varies from level to gently undulating. Three study plots within the area were selected for the experimental field trials (Figure 1).

2.1 Long Lake Experimental Spray Block

The Long Lake experimental spray block (54° 17', 101° 28') is located approximately 0.75 kilometres south of Long (Barbe) Lake and approximately 50 kilometres north of The Pas. Access to the site is via the Atik (Sturgeon Landing) Road approximately 6 kilometres west of PTH #10. The experimental spray block consisted of approximately eleven hectares within a larger zone that had been cutover in 1980 (D. Waugh*, pers. comm.). The cutover was planted with 3 year old white spruce stock in 1982. Deciduous regrowth, primarily aspen, birch and willow, was fairly dense and averaged 2 to 3 metres in height.

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* D. Waugh, Forester, Woodlands Division, Manfor Ltd.

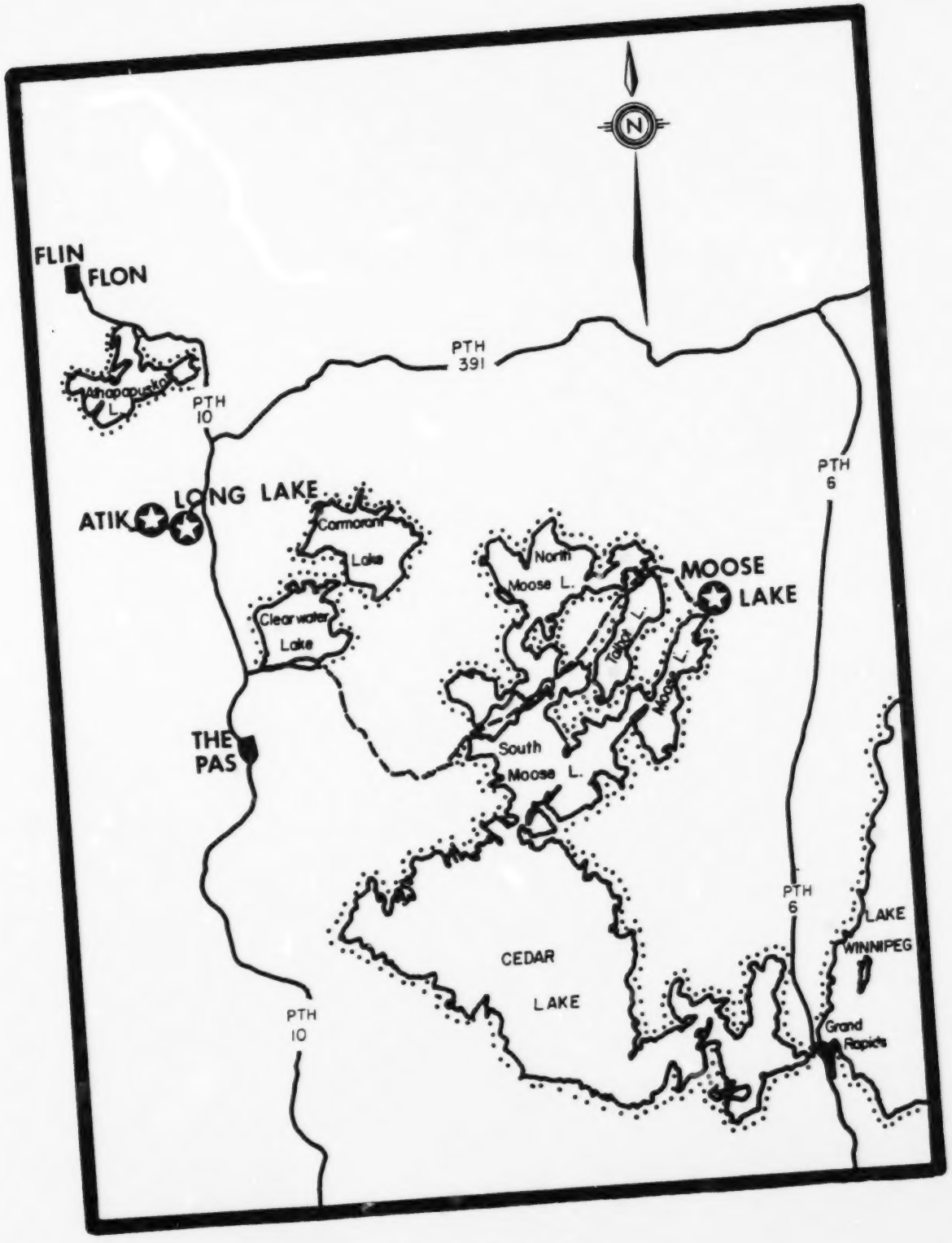

Figure I: Overview of the study area.

There were no natural waterbodies located within the experimental spray block (Figure 2) and even many of the peripheral sampling points were artificially created temporary ponds. A total of eleven sites were sampled, only one of which (site #L-5) was located within the experimental spray block. General characteristics of each pond sampled and proximity to the nearest boundary of the spray block are detailed in Table 1.

2.2 Atik Experimental Spray Block

The Atik experimental spray block (54° 17', 101° 29') is located approximately 7 kilometres west of the Long Lake block. It is accessed directly from the Atik (Sturgeon Landing) Road. The experimental spray block consisted of approximately 13 hectares within a larger zone that had been cutover in 1969 (D. Waugh, pers. comm.). Like the Long Lake cutover, the Atik site had also been planted with 3 year old white spruce stock in 1982. Some natural conifer regeneration had occurred but deciduous regrowth was particularly dense.

There were neither natural waterbodies nor artificial depressions holding water within the experimental spray block (Figure 3). A total of five sites nearby were sampled. General characteristics and proximity to the nearest boundary of the spray block are again detailed in Table 1.

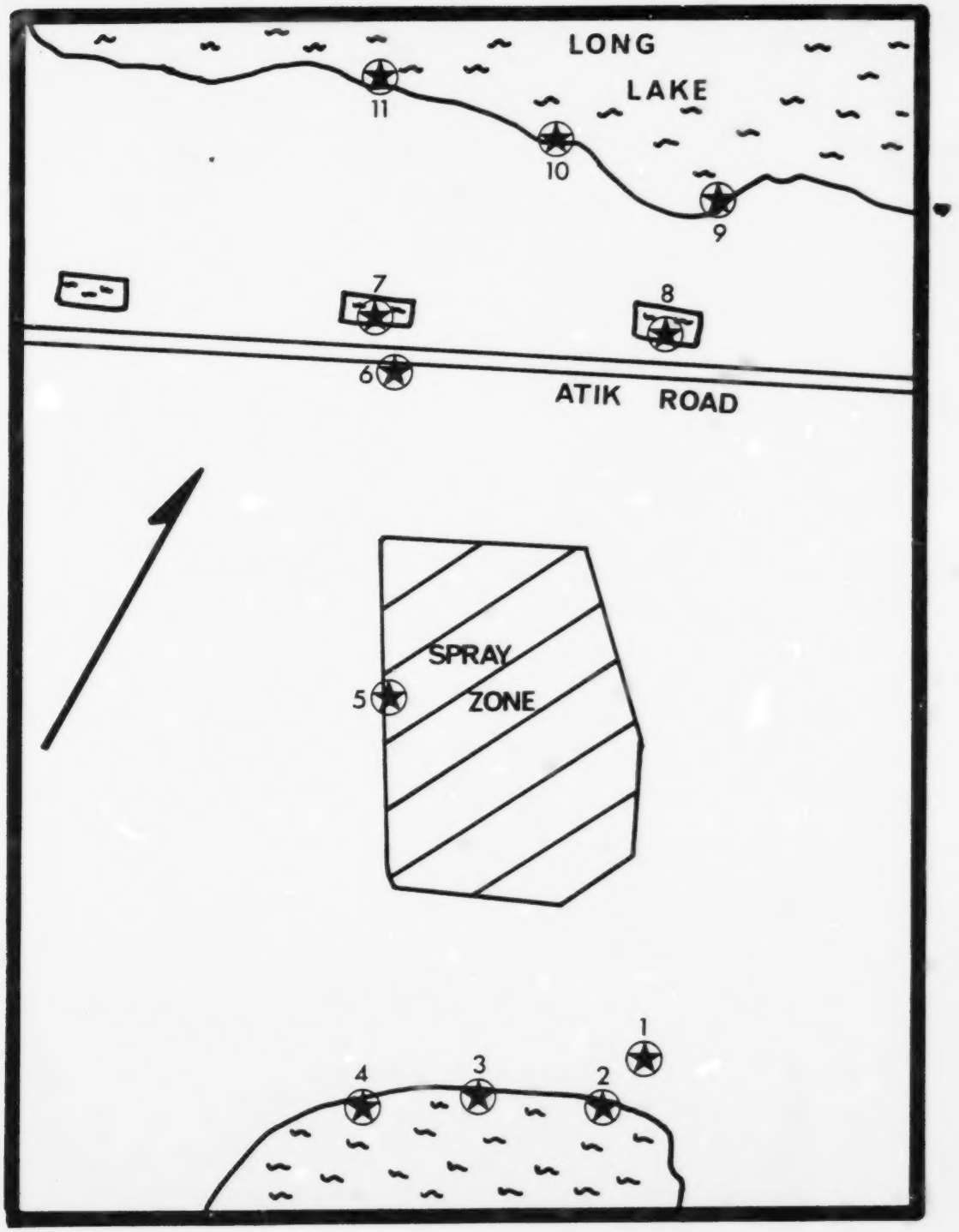

Figure 2: The Long Lake experimental spray block. (Not drawn exactly to scale; distances are listed in Table I.)

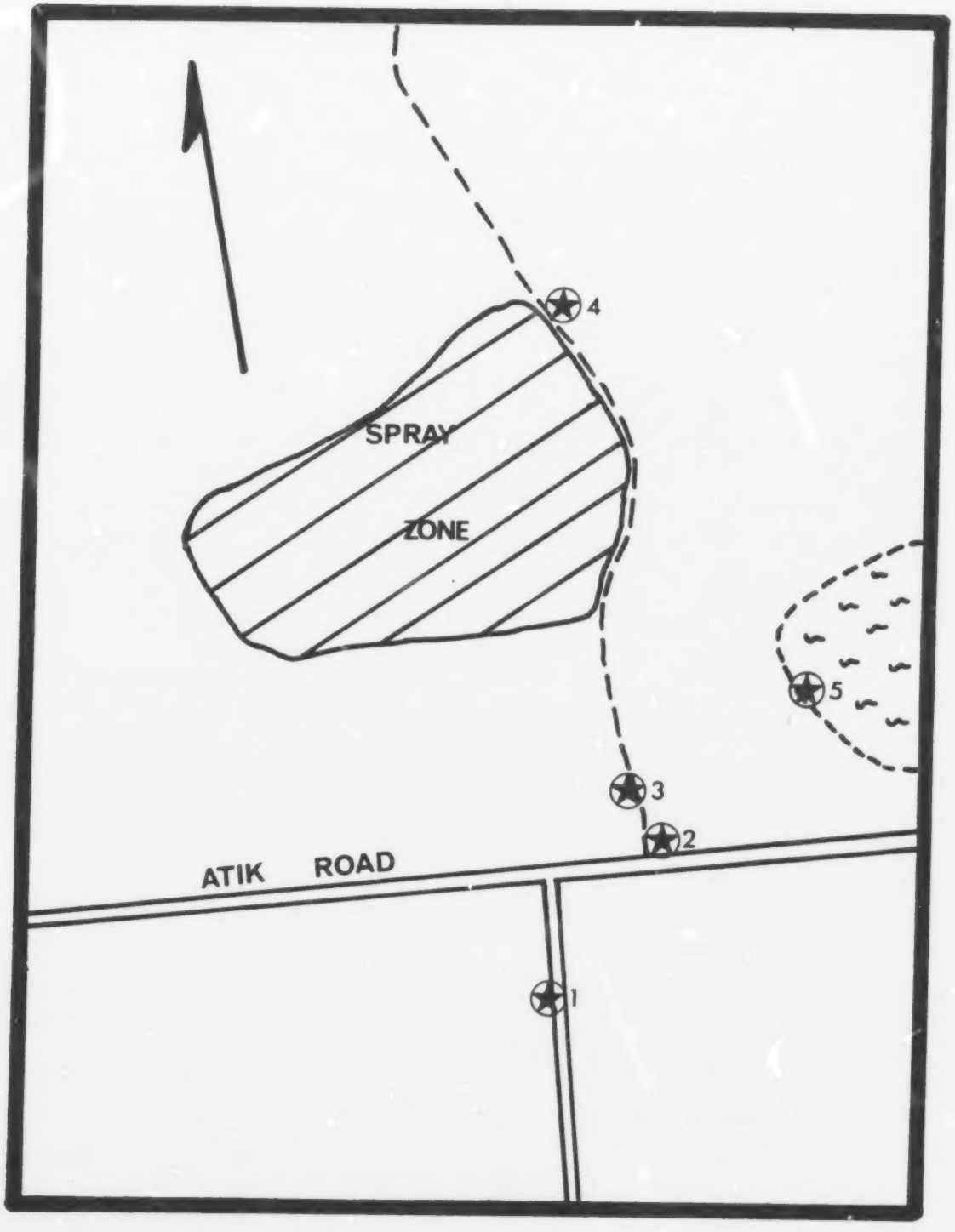

Figure 3: The Atik experimental spray block. (Not drawn exactly to scale; distances are listed in Table 1.)

TABLE 1: CHARACTERISTICS OF SAMPLING SITES

SITE*	ORIGIN	AREA	MAXIMUM DEPTH	APPROXIMATE DISTANCE TO NEAREST BOUNDARY OF SPRAY BLOCK
L-1	artificial borrow pit	5.3 x 4.2 m	0.50 m	185 m
L-2	natural lake (unnamed)	>1.0 ha	>3 m	235 m
L-3	natural lake (unnamed)	>1.0 ha	>3 m	250 m
L-4	natural lake (unnamed)	>1.0 ha	>3 m	285 m
L-5	artificial borrow pit	5.0 x 3.2 m	0.48 m	0 m
L-6	artificial, roadside ditch	7.0 x >30 m	0.45 m	215 m
L-7	artificial borrow pit	>30 x 30 m	0.8 m	285 m
L-8	artificial borrow pit	>30 x 30 m	0.6 m	325 m
L-9	natural lake (Long Lake)	>1.0 ha	>6 m	485 m
L-10	natural lake (Long Lake)	>1.0 ha	>6 m	550 m
L-11	natural lake (Long Lake)	>1.0 ha	>6 m	600 m
A-1	artificial, roadside ditch	3.0 x 27 m	0.30 m	500 m
A-2	artificial, roadside ditch	8.0 x >30 m	0.40 m	300 m
A-3	artificial borrow pit	5.0 x 3.7 m	0.60 m	205 m
A-4	artificial borrow pit	5.8 x 4.7 m	0.45 m	10 m
A-5	natural bog	>1.0 ha	>1.0 m	300 m
M-1	natural pond (unnamed)	>1.0 ha	>2.0 m	730 m
M-2	natural wet site	>30 x 30 m	0.35 m	45 m
M-3	artificial borrow pit	5.7 x 5.2 m	0.25 m	45 m
M-4	artificial borrow pit	15 x 5 m	0.6 m	450 m

* Sites of the Long Lake, Atik and Moose Lake experimental spray blocks are designated by the prefixes "L", "A" and "M", respectively.

2.3 Moose Lake Experimental Spray Block

The Moose Lake experimental spray block (54° 05', 99° 34') is located approximately 8 kilometres east of the northeast arm of South Moose Lake and approximately 115 kilometres east of The Pas. Access to the site is via Manfor's William Lake forestry haulage road off the provincial Moose Lake road. The experimental spray block consisted of approximately 40 hectares within a larger zone that had been cutover in the spring of 1984 (D. Waugh, pers. comm.). The site had not been planted and regrowth was minimal.

Apart from wheel ruts, ponded water was not present within the experimental spray block (Figure 4), Only 4 sites were sampled, one of which (M-1) was a natural pond constituting the headwaters of the Minago River system. General pond characteristics and proximity to the nearest boundary of the spray block are detailed in Table 1.

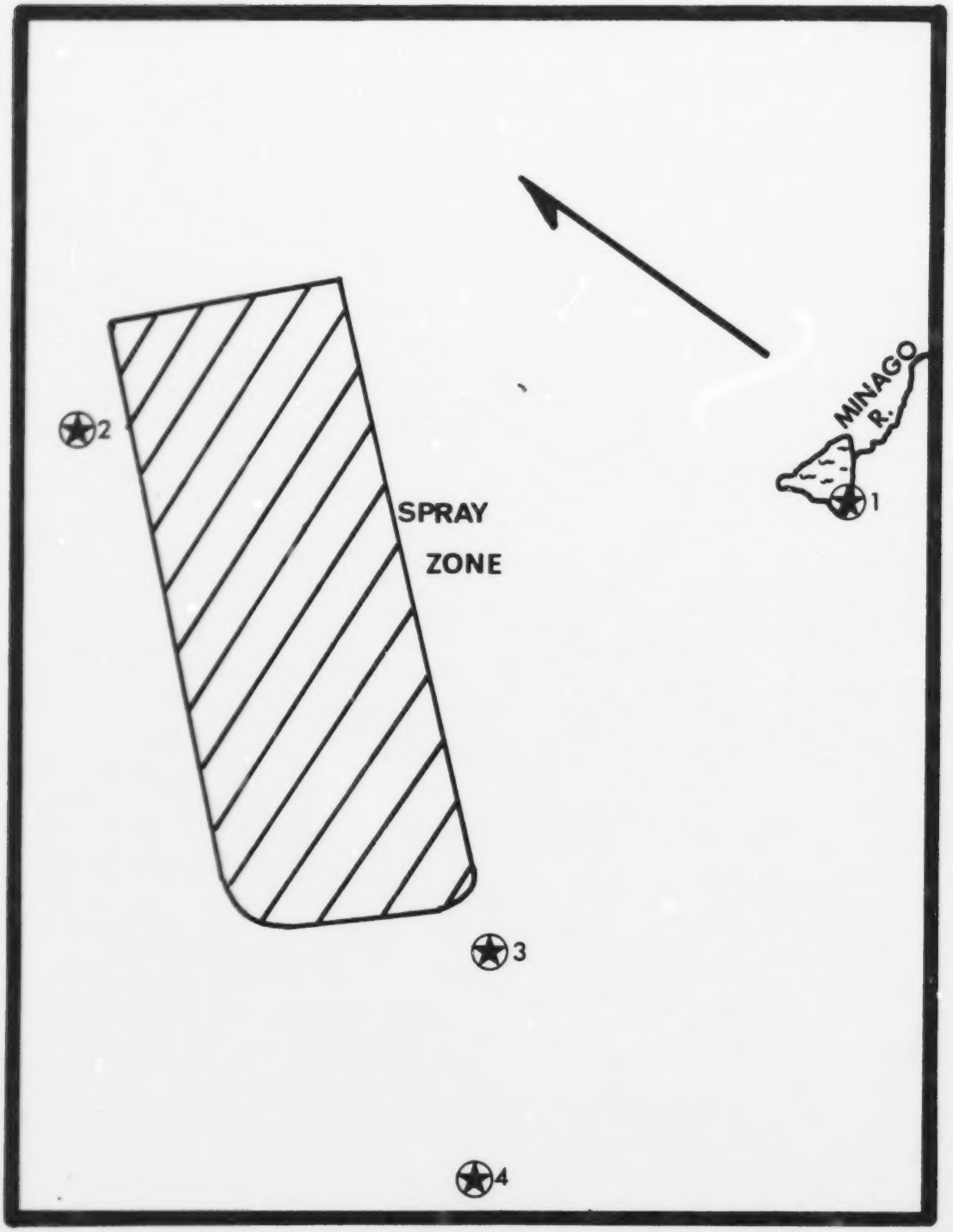

Figure 4: The Moose Lake experimental spray block. (Not drawn exactly to scale; distances are listed in Table I.)

3.0 METHODS

3.1 Rationale

Proper sampling strategy, which requires an adequate number of replicates per treatment, was severely hampered by the reality of site conditions. Limited ponded water located within the experimental spray blocks was available. Hence, accelerated sampling frequency was adopted as a surrogate for site replication.

'What to measure' is always an important consideration when monitoring any biocide. This is because some short lived compounds may have persistent and even more toxic breakdown products than the parent compound. Thus it was essential to know which degradation products might be expected in order to more effectively achieve study goals. The literature indicated that the principle metabolite encountered is aminomethylphosphonic acid, or AMPA (Rueppel et al, 1977). Several other metabolites are minor (i.e. they occur at amounts less than 1% of the glyphosate applied) or can develop only under certain conditions (Torstensson, 1985). The end products, derived either directly from glyphosate or the metabolites, are a variety of natural products including carbon dioxide, animo acids, phosphonic acids and phosphates (Rueppel et al, 1977; Coupland, 1985). Given this background, analytical resources were focused on glyphosate and AMPA.

Analytical accuracy is of paramount concern when monitoring objectives include either quantitation or persistence. Since local facilities with glyphosate analytical capabilities were not available within Manitoba, reliance had to be placed on a reputable laboratory

not under the control of Manitoba Environment and Workplace Safety and Health. Therefore, it was deemed prudent to independently assess analytical accuracy by submitting a series of blind spikes and controls.

3.2 Field Methods

Analytical personnel had advised that it was preferable to use plastic containers for sample collection and submission. This was due to a lower propensity for product adherence to container walls than might be encountered with glass materials (S. Stupp, pers. comm.*). Accordingly, new, one litre poly bottles were triple rinsed on site and filled to within 3 cm of the top by immersion at approximately 5-10 cm below the surface. Samples were stored on ice until transfer to freezing facilities. Samples were maintained in a frozen state until delivery to the analytical laboratory.

Literature available prior to the study indicated that glyphosate dissipated in non-flowing ponds at a rate which follows first order kinetics (Sacher, 1978). Its half-life was estimated at approximately 12 days (Ibid). However, extrapolation of data from exposed streams (Newton et al, 1984) indicated the possibility of a somewhat shorter half-life but a precise determination was precluded by

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* S. Stupp, formerly Director of Pesticides Chemistry, Wastex Industries Inc.; Pottstown, Pennsylvania; currently Director of Pesticide Chemistries, A & S Environmental Testing, Inc.; Temple Pennsylvania.

uncertainties attributable to flow rates. The differences in the literature and the uncertainties which might be caused by a more northerly climate, prompted sampling within 1 1/2 hours of herbicide application and at intervals of two days, five days, thirty days and nine months thereafter. Following receipt and preliminary assessment of analytical data to the thirty day interval, plans for sampling at the nine month interval were discontinued.

3.3 Analytical Methods

Analytical services were provided under contract by Wastex Industries, Inc. of Pottstown, Pennsylvania, USA. The procedure followed was entitled "Analytical Residue Method for N-(Phosphonomethyl) Glycine and Aminomethlyphosphonic Acid in Water" (S. Stupp, pers. comm.). Water samples were eluted through Chelex 100 resin in the Fe^{+++} form in order to isolate the compounds of interest (Ibid). Glyphosate and AMPA were then eluted from the resin with hydrochloric acid, iron was removed using an anion exchange resin, the samples were concentrated to dryness to remove the hydrochloric acid, and were then analyzed using a Fluorometer with a post-column reaction system (Ibid).

As previously indicated, analytical accuracy was independently assessed by submission of blanks and spikes. Blanks presumably containing no herbicide were obtained from all sample sites prior to glyphosate application. Statistical analysis

of results permitted evaluation of the lower limits of detection. Spiked samples were provided by quality assurance staff of the W. M. Ward Technical Services Laboratory in Winnipeg. Spikes were prepared by dilution of commercial Roundup(R) with doubly distilled water (L. Prokopanko,* pers. comm.). These were submitted as samples from sites which had dried up prior to completion of the thirty day sampling interval. Results from spiked samples permitted evaluation of analytical accuracy for glyphosate. Analytical capabilities for AMPA were not independently assessed because stock chemical could not be obtained.

3.4 Herbicide Application

The herbicide mix was aerially applied with a Bell-47 helicopter equipped with a horizontal spray boom. Applications were made to the Long Lake and Atik experimental spray blocks on August 22, 1985. The Moose Lake block was sprayed on August 23, 1985. Atmospheric conditions prevalent during applications are described separately by Phillips (in prep.). The rates of application for the Long Lake, Atik and Moose Lake blocks were estimated at 3.0, 4.0 and 5.0 litres of commercial Roundup(R) formulation per hectare, respectively (D. Waugh, pers. comm.). This corresponded to 1.08, 1.44 and 1.80 kg of active ingredient (i.e. glyphosate) per hectare**.

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* L. Prokopanko, Chemist, Quality Assurance Section; W.M. Ward Technical Services Laboratory, Winnipeg, Manitoba.

** Commercial formulations contain 360 g active ingredient per litre (McWhorter and Derting, 1985).

4.0 RESULTS AND DISCUSSION

4.1 Analaytical Capabilities

Wastex Industries, Inc. had reported detection capabilities down to the 1.0 µg/L level for both glyphosate and AMPA residues in water (S. Stupp, pers. comm.). However, among the twenty blank samples submitted, three detections were reported for each of glyphosate and AMPA (Table 2). The mean of reported glyphosate values were 1.50 $\pm$ 0.36 µg/L. Establishment of 95% confidence intervals about the mean (i.e. $\pm 2\ \sigma$) permitted a crude estimation of a calculated detection limit at 2.2 µg/L for glyphosate (Figure 5). This value was considered the limit below which reported detections would not be accepted as valid detections. The calculated detection limit derived in the present study was remarkably similar to the standard Monsanto limit of 2.5 µg/L (Sacher, 1978). Therefore, only detections of glyphosate at or above the 2.2 µg/L level were considered valid in the present study.

AMPA residues reported from blanks submitted (Table 2) had a mean of 3.80 $\pm$ 2.62 µg/L (Figure 5). Though substantially greater than the 1.0 and 2.5 µg/L limits reported by Wastex Industries, Inc. (S. Stupp, pers. comm.) and Sacher (1978), respectively, the 9.05 µg/L value obtained during the present study was nevertheless adopted.

The second aspect to be considered during assessment of analytical capabilities, concerned recovery rates. Wastex Industries, Inc. internal quality control program had reported glyphosate

TABLE 2: ANALYTICAL RESULTS FOR BLANK AND SPIKED SAMPLES SUBMITTED INCOGNITO

Nature of Sample	Apparent Glyphosate (µg/L)	True Glyphosate (µg/L)	Apparent AMPA (µg/L)	True AMPA (µg/L)
Blank (L-1)	<1.0	<1.0	<1.0	<1.0
Blank (L-2)	1.8	<1.0	6.2	<1.0
Blank (L-3)	<1.0	<1.0	<1.0	<1.0
Blank (L-4)	<1.0	<1.0	<1.0	<1.0
Blank (L-5)	<1.0	<1.0	<1.0	<1.0
Blank (L-6)	<1.0	<1.0	<1.0	<1.0
Blank (L-7)	<1.0	<1.0	<1.0	<1.0
Blank (L-8)	<1.0	<1.0	<1.0	<1.0
Blank (L-9)	<1.0	<1.0	<1.0	<1.0
Blank (L-10)	<1.0	<1.0	<1.0	<1.0
Blank (L-11)	<1.0	<1.0	1.0	<1.0
Blank (A-1)	<1.0	<1.0	<1.0	<1.0
Blank (A-2)	<1.0	<1.0	<1.0	<1.0
Blank (A-3)	<1.0	<1.0	<1.0	<1.0
Blank (A-4)	<1.0	<1.0	<1.0	<1.0
Blank (A-5)	<1.0	<1.0	<1.0	<1.0
Blank (M-1)	1.6	<1.0	<1.0	<1.0
Blank (M-2)	<1.0	<1.0	<1.0	<1.0
Blank (M-3)	1.1	<1.0	4.2	<1.0
Blank (M-4)	<1.0	<1.0	<1.0	<1.0
Spike	<1.0	<1.0	-	-
Spike	8.7	7.58	-	-
Spike	28.9	23.7	-	-
Spike	95.3	74.9	-	-

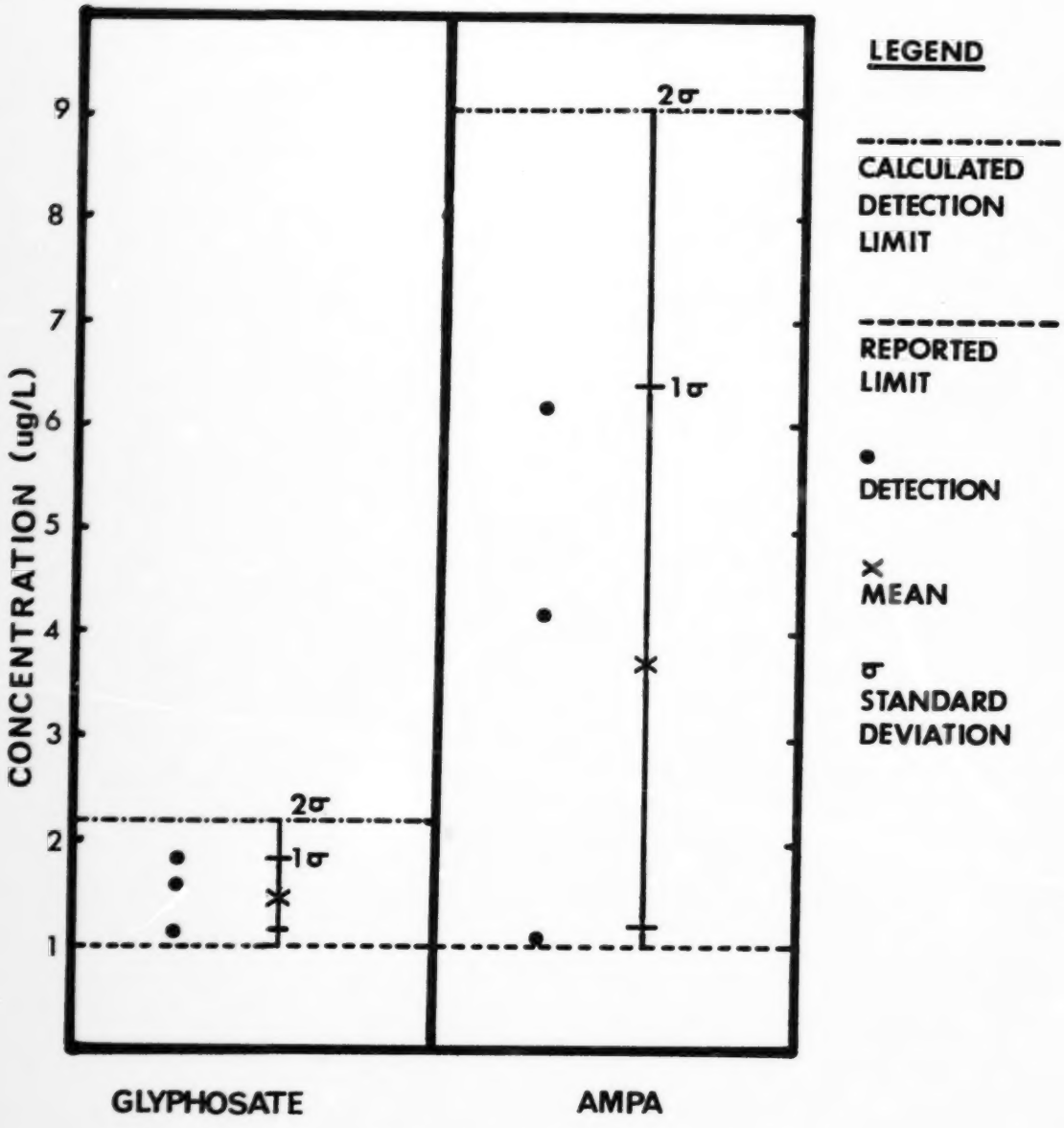

Figure 5: Determination of calculated detection limits from reported glyphosate and AMPA detections in blank samples.

recoveries ranging from 71% to 106% with a mean of 96% (Figure 6). Recovery rates obtained for spiked samples ranged from 100% to 127% with a mean of 115% (Figure 6). This meant that values reported by Wastex Industries Inc. may have been overestimated by approximately 19%. However, the analytical values obtained were not corrected for the apparent positive bias and, instead, are presented in the present study as reported by the analytical facility*. This approach avoided the potential danger of residue underestimation.

Inability to obtain stock chemical precluded an independent evaluation of the Wastex Industries Inc. reported recovery rate of 85% for AMPA.

4.2 Residues

Analytical results as reported by the analytical facility are detailed in Tables 3 and 4.

4.2.1 Quantitation

Glyphosate residues were detected at four locations during the thirty day sampling period (Table 3). Maximum residues of 1088 µg/L were detected at site L-5 (Figure 2), the only sampling site located within an experimental spray block. Although this was

* Note that values below the calculated detection limited are not reported.

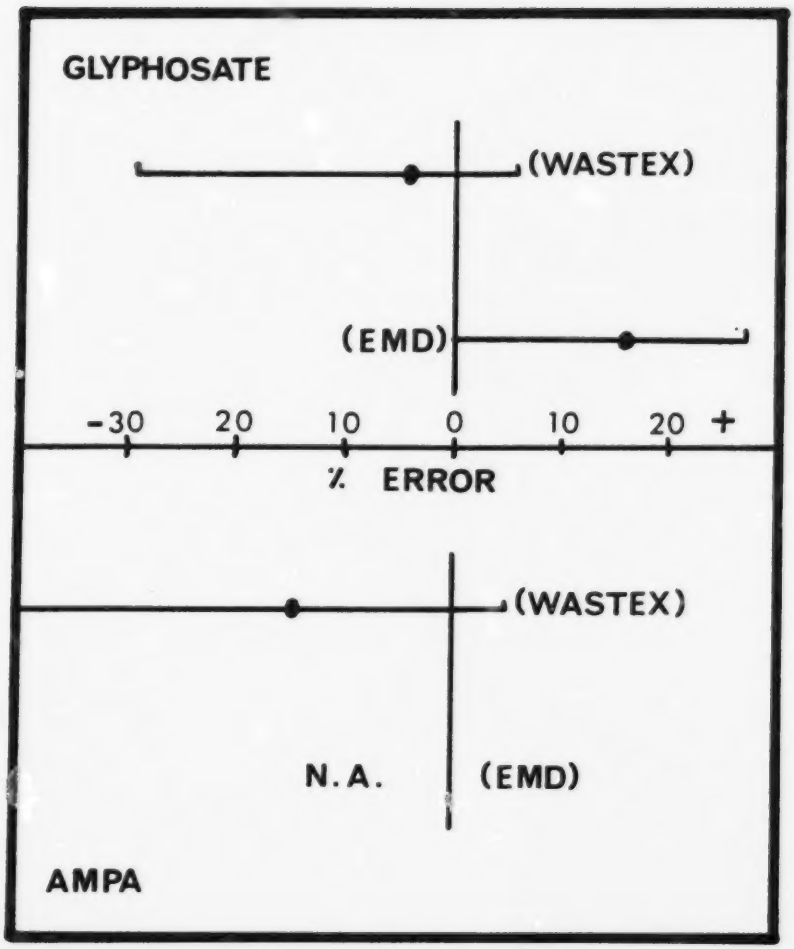

Figure 6: Range of glyphosate and AMPA recovery rates reported by Wastex Industries Inc. (WASTEX) and by the present study (EMD).

TABLE 3: GLYPHOSATE ANALYTICAL RESULTS FOR THE LONG LAKE, ATIK AND MOOSE LAKE EXPERIMENTAL SPRAY BLOCKS

	GLYPHOSATE RESIDUES (µg/L)* AT VARIOUS INTERVALS AFTER SPRAY			
SAMPLE SITE	1.5 hours	2 days	5 days	30 days
Long Lake 1	ND	ND	ND	ND
Long Lake 2	ND	ND	ND	ND
Long Lake 3	ND	ND	ND	ND
Long Lake 4	ND	ND	ND	ND
Long Lake 5	1088	149	55.5	ND
Long Lake 6	ND	ND	ND	ND
Long Lake 7	ND	ND	ND	ND
Long Lake 8	ND	ND	ND	ND
Long Lake 9	ND	ND	ND	ND
Long Lake 10	ND	ND	ND	ND
Long Lake 11	5.3	ND	ND	ND
Atik 1	ND	ND	DRY	DRY
Atik 2	ND	ND	ND	ND
Atik 3	ND	ND	DRY	DRY
Atik 4	ND	11.3	DRY	DRY
Atik 5	ND	ND	ND	ND
Moose Lake 1	ND	ND	ND	ND
Moose Lake 2	ND	ND	ND	ND
Moose Lake 3	18.8	33.0	32.5	DRY
Moose Lake 4	ND	Sample Lost	ND	ND

* "ND" indicates values less than the 2.2 µg/L calculated limit of detection; "DRY" indicates that the sample site held no water at time of sampling.

TABLE 4: AMPA ANALYTICAL RESULTS FOR THE LONG LAKE, ATIK AND MOOSE LAKE EXPERIMENTAL SPRAY BLOCKS

	AMPA RESIDUES (µg/L)* AT VARIOUS INTERVALS AFTER SPRAY			
SAMPLE SITE	1.5 hours	2 days	5 days	30 days
Long Lake 1	ND	ND	ND	ND
Long Lake 2	ND	ND	11.9	ND
Long Lake 3	ND	ND	10.7	ND
Long Lake 4	ND	ND	ND	ND
Long Lake 5	9.8	ND	10.9	ND
Long Lake 6	ND	ND	ND	ND
Long Lake 7	ND	ND	ND	ND
Long Lake 8	ND	ND	ND	ND
Long Lake 9	ND	ND	ND	ND
Long Lake 10	ND	ND	ND	ND
Long Lake 11	ND	ND	ND	ND
Atik 1	ND	ND	DRY	DRY
Atik 2	ND	ND	ND	ND
Atik 3	ND	ND	DRY	DRY
Atik 4	ND	ND	DRY	DRY
Atik 5	ND	ND	ND	ND
Moose Lake 1	ND	ND	ND	ND
Moose Lake 2	ND	ND	ND	ND
Moose Lake 3	ND	ND	44.7	DRY
Moose Lake 4	ND	ND	ND	ND

* "ND" indicates values less than the 9.05 µg/L calculated limit of detection; "DRY" indicates that the sample site held no water at time of sampling.

approximately double, the 540 µg/L calculated expected value*, it was not unreasonable given the consistency of results over time, the uncertainties of aerial application and pond volume estimation, the possibility of a 19% positive analytical bias and the extreme unlikelihood that complete mixing had occurred prior to sample collection (i.e. within 1.5 hours of pesticide application). Thus the value of 1088 µg/L was considered a valid quantitation of glyphosate residues within the Long Lake experimental spray block.

Glyphosate residue detection at a second Long Lake site (i.e. site L-11; Figure 2) appeared to be spurious. This was because it was unsupported by detections at nearby sites (i.e. no detections at sites L-6, L-7, L-8, L-9 and L-10; Figure 2) and further detections of either glyphosate or AMPA at site L-11 were not made later in the sampling schedule (Tables 3 & 4).

Glyphosate residue detection at one Atik site (site A-4; Figure 3) two days after herbicide application appeared valid because of proximity to the spray zone boundary (10 M; Table 1) and because reported residues (11.3 µg/L, Table 3) were well above the 2.2 µg/L calculated limit of detection. However, independent support was not available since residues of glyphosate and/or AMPA were not detected within one and one-half hours of pesticide application, AMPA residues were not detected concurrently on day 2 of

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* Given a rate of application of 1.08 kg/hectare, pond surface area of 16 M^2 (from Table 1) pond volume of 3.2 M^3 (calculated from Table 1 according to Hutchinson, 1957) and assuming complete and instantaneous mixing, the calculated expected value was (1.08×10^9 µg x 1.6×10^{-3} ha/3.2×10^3L) = 540 µg/L.

sampling and because the pond dried up prior to the following sampling interval (i.e. day 5).

Glyphosate residues were consistently detected (Table 3) at site M-3 (Figure 4) near the Moose Lake experimental spray block. However, given the comparatively low values obtained during the initial sampling period (i.e. 18 µg/L at 1.5 hours versus 33.0 µg/L at 2 Days; Table 3), the initial quantitation may be viewed with circumspection. In any event, since site M-3 was located approximately 45 M beyond the boundaries of the block (Table 1), the quantitation recorded was not indicative of residues which might have occurred within the spray block it self.

AMPA residues were characterized by inconsistent detections (Table 4) and interpretation was plagued by apparently spurious*, low level detections at sites L-2 and L-3 (Figure 2). Nevertheless, detection of AMPA residues at sites L-5 and M-3 (Figures 2 and 4, respectively) confirmed that metabolism of glyphosate had occurred at both the Long Lake and Moose Lake experimental spray blocks. The ratio of maximum AMPA residues to maximum glyphosate residues could be calculated only for site L-5 since initial quantitations for site M-3 were considered suspect. The ratio derived during the present study (0.010) was considered acceptable when compared to ratios extracted from the work of Tooby (1985), Wan (1986) and Newton et al (1984), (i.e. 0.024, L 0.05 and 0.21; respectively).

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* Detections at sites L-2 and L-3 were considered spurious because of proximity to the 9.05 µg/L calculated detection limit and because the single instances were not supported by further AMPA detections or by any glyphosate detections

4.2.2 Persistence

Data suitable for assessment of persistence was derived from Long Lake site L-5 (Table 3, Figure 4). Optimal curve fitting indicated that the rate of glyphosate residue dissipation (Figure 7) could be described as following an exponential (r^2 = 0.88), a logarithmic (r^2 = 0.89) or even a power curve (r^2 = 0.89) relationship. A half-life varying from approximately eight hours to approximately fifteen hours was predicted from the preliminary regressions. However, a minimal number of data points (N=4) and the absence of replicates caution against a precise definition of dissipation kinetics from the present study. Rather, it was considered more accurate to conclude that the half-life for glyphosate applied to local waters and under local conditions was less than twenty-four hours.

Although very little pertinent literature was available, all but one reference (Sacher 1978) indicated that glyphosate residues dissipate from static waters at a much slower rate than suggested by the present study. Sacher's (1978) work suggested a half-life of approximately 12 days. Frazier's research efforts (cited in Bronstad and Friestad, 1985) suggested glyphosate residues were somewhat more persistent as a 63% reduction occurred only after 63 days. Malik (cited in Tooby, 1985) achieved similar results when he found that 50% degradation occurred in 7 weeks. However, each of these studies involved the transfer of natural waters to an artificial setting. Field studies were apparently minimal and restricted to that of Mestdagh (cited in Tooby, 1985), who applied Roundup (R)

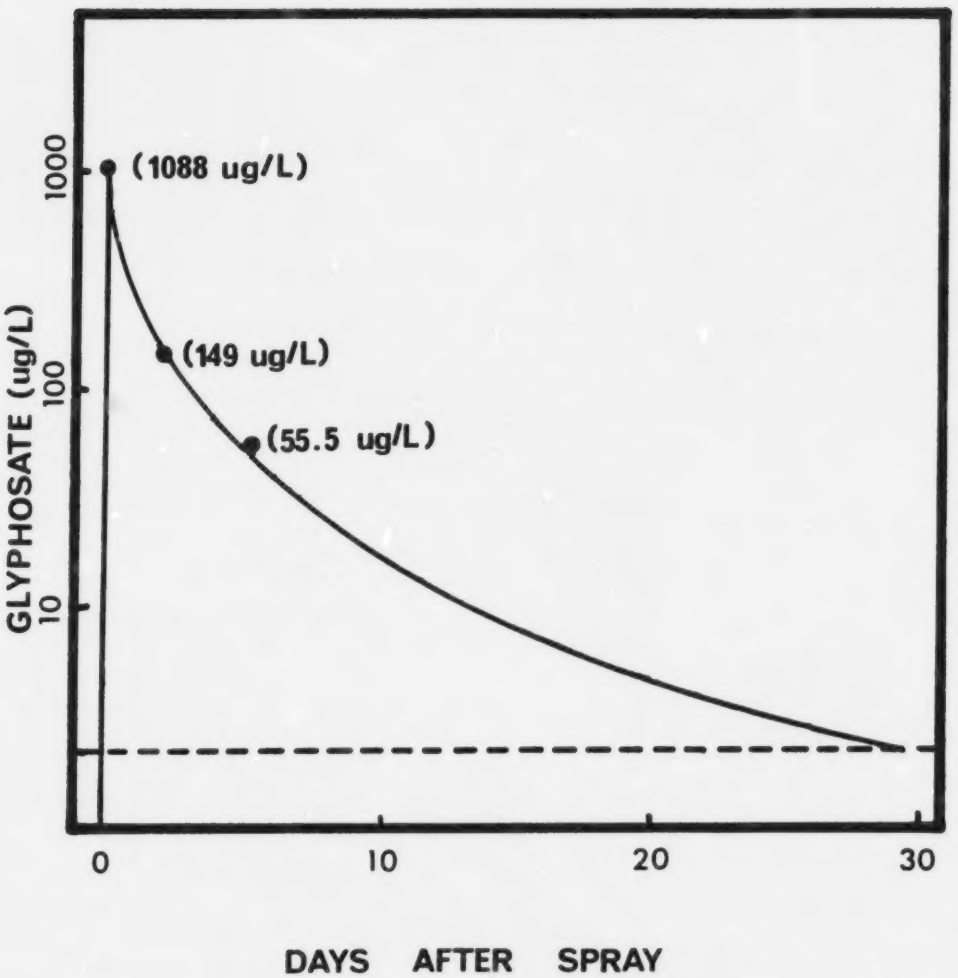

Figure 7: Dissipation rate of glyphosate residues at Long Lake experimental spray block site L-5.

(3.6 kg active ingredient/ha) to a pond 30 cm deep. He found an initial half-life of less than 4 hours; thereafter the half-life approximated 12 hours (Ibid). These data supported what might otherwise be considered radical results of the present study. Apparently, field dissipation rates for glyphosate residues do not closely parallel results obtained in laboratory studies.

Dissipation rates for AMPA could not be estimated due to infrequent detection of residues. However, residues were detected five days after Roundup(R) application but were not detected at the 30 day sampling interval.

4.2.3 Mobility

Nineteen of the twenty sampling sites were located beyond the boundaries of the experimental spray blocks and were therefore suitable for assessment of mobility under local conditions. Among these sites, reliable glyphosate detections were recorded for only two stations, A-4 of the Atik block (Figure 3) and M-3 of the Moose Lake block (Figure 4). (Detection at a third site, L-H, was considered spurious.) Given the 10m proximity to the boundary of the spray block, the occurrence of residues at site A-4 appeared to be a case of drift following aerial application. Near atmospheric inversion conditions developed during herbicide application (Phillips, pers. comm.*) and may explain why residues were not detected during

* F. Phillips, Soils and Vegetation Specialist, Terrestrial Standards and Studies Section; Manitoba Environment and Workplace Safety and Health.

the initial post spray sampling period. Samples at A-4 were collected approximately 20 minutes after completion of aerial application and the full dosage of herbicide droplets likely had not settled prior to sampling.

Given the 45 m proximity to the boundary of the spray block and occasional, forceful westerly gusts during aerial herbicide application, detection of glyphosate residues at site M-3 indicated drift during herbicide application. Indications of drift during application at the Moose Lake experimental spray block were also obtained by Phillips (pers. comm.) during a concurrent study of residues in vegetation and soils.

Evidence of export of glyphosate residues by means other than aerial drift during or immediately following aerial application was not obtained during the present study. Although Wan (1986) has reported short term export of glyphosate by streams following heavy rains, others reported that strong adsorption to soil constituents and silt particles rapidly and effectively inactivate glyphosate (Sprankle et al, 1975; Sacher, 1978; Bronstad and Friestad, 1985; Tooby, 1985). Therefore it was concluded that under local conditions, aerial drift during or immediately following Roundup $^{(R)}$ application was the only significant mechanism for glyphosate export beyond the target area.

Reliable AMPA residues were detected only once (site M-3) beyond the confines of the experimental spray blocks. This did not permit assessment of AMPA mobility under local conditions.

5.0 Conclusions

1. Initial maximum glyphosate residues detected in water from a pond within an experimental spray block corresponded reasonably well to an estimate calculated from the rate of application, pond surface area and pond volume.

2. Maximum glyphosate residues of 1088 µg/L in pond water was a valid quantitation for the Long Lake experimental spray block.

3. The half-life for glyphosate aerially applied as the commercial formulation Roundup (R) to local surface waters and under local conditions was less than 24 hours. This rate of dissipation may variedly be described as following an exponential, a logarithmic or a power curve relationship.

4. Under local conditions encountered in this study, aerial drift during or immediately following Roundup (R) application was the only significant mechanism for export of glyphosate beyond the target area.

5. Infrequent detections of AMPA residues precluded definitive statements regarding quantitation, persistence and mobility under local study conditions.

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